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Preparation and characteristics of vanadium oxide thin films by controlling the sputtering voltage

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ABSTRACT

Influence of sputtering voltage on the deposition process and characteristics of vanadium oxide thin films prepared by reactive DC magnetron sputtering is investigated. The target surface cleaning is controlled by adjusting the sputtering voltage. During the sputtering process, the sputtering voltage increases faster with larger O_2 gas flow rate. The sputtering voltage is easy to be stable with larger sputtering voltage. The measured sputtering voltage is correlated to the ion induced secondary electron emission (ISEE) coefficient of the target material. The ISEE coefficient of the oxidized vanadium target surface is lower than the ISEE coefficient of the vanadium metal. The semiconductor to metal (S–M) phase transition temperature decreases with the sputtering voltage, leading to the lower the corresponding temperature of the maximum temperature coefficient of resistance (*TCR*). By this way, O/V ratio, *R*, and *TCR* of VOx films can be controlled by adjusting the sputtering voltage.

1. Instruction

As a special functional material, vanadium oxide thin films have been studied extensively due to their attractive physical and chemical properties [1–3]. They have been used in many technological applications, such as in memory materials [4], all-optical switching devices [5], micro-batteries [6], photovoltaics [7], terahertz imaging [8], and thermistor bolometer [9,10]. The principal oxides of vanadium, occur as single valence oxide, are in the form of VO, V_2O_3, VO_2, and V_2O_5. However, the vanadium–oxygen phases also include mixed valences oxides containing two or more oxidation states [11]. Some vanadium oxides with certain V/O ratio and certain vanadium valence undergo the phase transition from semiconductor to metal (S–M) with significant variation in structural, optical and electrical properties as they exceed a critical temperature T_c. Among these vanadium oxides, VO_2 has attracted much attention due to its perfect electrics and optics properties. As a heat-sensing material with low S–M phase transition temperature (68 °C), VO_2 has a promising prospect in infrared imaging, and provides a wide range application in military and medical service.

Reactive dc magnetron sputtering is one of the methods widely used to prepare vanadium oxide thin films. O_2 is used as reactive gas to deposit the thin films with sputtering the pure target. The reaction mechanisms between the sputtered vanadium and the reactive gas suffers instable problem, especially for the preparation of VOx films [11]. In many cases, the main reason is the oxidation takes place at the surface of the vanadium target. To avoid the effects from experimental conditions, i.e., the target current, the sputtering pressure, and the magnetic field, the control of target voltage is a feasible way to regulate the target oxidation with a constant target current mode [12].

In our previous work, reactive magnetron-sputtering in constant current mode in a vanadium-O_2/Ar system was simulated by adopting both kinetics model and Berg's model, and concluded that the presented theoretical models for parameter-dependent case and time-dependent case can be used to comprehend the target voltage behavior in the deposition of vanadium oxide thin films [13,14]. In this paper, we report the detailed study of the influence of sputtering voltage on the deposition process characteristics of VOx thin films. By adjusting the sputtering voltage, VOx thin film samples are prepared and characterized to verify the control of sputtering voltage is a feasible approach to obtain VOx thin films with different properties.

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2. Experiment apparatus and procedure

Vanadium oxide thin films were deposited by reactive DC magnetron sputtering in a planar magnetron sputtering system, as shown in Fig. 1. The magnetron sources are placed at a distance of ~55 mm from the substrate (substrate center to target surface center) and tilted 30° away from the substrate normal. The target material was a bulk vanadium disk (80 mm in diameter) with a high purity of 99.99 wt%. The substrates were single crystal silicon slice (P(100)) with silicon nitride thin film layer.

X-ray photoelectron spectroscopy (XSAM800) was used to obtain detail information regarding to the composition of the films. Thermal resistance of the films was measured by four-point resistivity technique. In the experiment, depositions were performed at the basic pressure of 2×10^{-3} Pa. During the deposition, the target current was constant and kept at 0.38 A. The substrate temperature was 300 °C. The details of experimental process are as follows: (1) Obtaining basic vacuum of 2×10^{-3} Pa. (2) Cleaning the vanadium target surface by pre-sputtering in pure Ar atmosphere with constant flow of 118 sccm (sccm: standard cubic centimeter per minute). (3) With constant Ar flow and O_2, reactive sputtering at different flow ratio of Ar/O_2 mixed conditions. In steps (2) and (3), small angle valves-7a was closed, and small angle valves-7b and 7c, big parallel slide valve-11 was opened. According to the process above, four cases with different O_2 reactive gas in chamber were studied, which were named as GA, GB, GC, and GD, and the corresponding to oxygen flows were at 2.4 sccm, 2.9 sccm, 3.4 sccm, and 4.5 sccm, respectively. Four VOx thin film samples were prepared by controlling the sputtering voltage at 326 V, 316 V, 306 V, and 286 V.

3. Results and discussions

3.1. Sputtering voltage behavior

In the process of vanadium oxide thin film, sputtering voltage influences obviously on the film properties. Therefore, it is necessary to study and ensure the evolution of the sputtering voltage behavior in different sputtering conditions. To exclude the possible influence from the other experimental parameters, i.e., the target current, the sputtering pressure, and the magnetic field, the experiments were repeated under different O_2 flow conditions. In the experiments, Ar flow was maintained at 118 sccm, and O_2 flow was at 2.4 sccm, 2.9 sccm, 3.4 sccm, and 4.5 sccm, respectively. An overview of the sputtering voltage behavior during the target pre-sputtering in single Ar gas condition and the subsequent co-sputtering in Ar/O_2 mixed conditions with O_2 flow above is given in Fig. 2. In this process, the O_2 flow was input instantaneously.

As shown in Fig. 2, the sputtering voltage indicates similar change behavior during the vanadium target pre-sputtering process in single Ar condition in the four cases with different O_2 flow. Once the ignition of discharge, which corresponding to the zero of abscissa in Fig. 2, the sputtering voltage is high, and then drops dramatically before it decreases slowly. This obviously dropping is attributed to the transient ionization of argon gas between the target and the substrate when the magnetic field is introduced, resulting in the plasma impedance between the target and the substrate decreases quickly. As observed above, the target current is constant; the sputtering voltage drops down dramatically. Then, the subsequent sputtering voltage is mainly related to the oxide layer, which is formed on the vanadium target surface in natural or during the plasma oxidation in last reactive sputtering experiment. During the sputtering process, the oxidation layer is gradually cleaned from the target surface, and the bottom pure vanadium element is exposed, which resulted in the enhancement of ISEE coefficient of the target. The plasma impedance decreases because the ISEE coefficient of vanadium metal is much larger than that of vanadium oxides. Because the target current is constant, this change of the plasma impedance exhibits in a sputtering voltage change. According to the well known Thornton relation, it is expected that the sputtering voltage is inversely proportional to the ISEE coefficient of the target material [15]. Then the sputtering voltage decreases slowly. With the vanadium target surface cleaned to be pure and return to the vanadium metallic state, the ISEE coefficient of the target surface came to be stable and the sputtering voltage changed little. The time to return to the metallic state will depend on the sputter yield of the formed oxide layer on target surface. The results demonstrate the target surface has been cleaned over as the sputtering voltage changed little.

In the four cases with different O_2 flow, as shown in Fig. 2, there exists difference of the sputtering voltage value during the target pre-sputtering in Ar condition, which was attributed to the

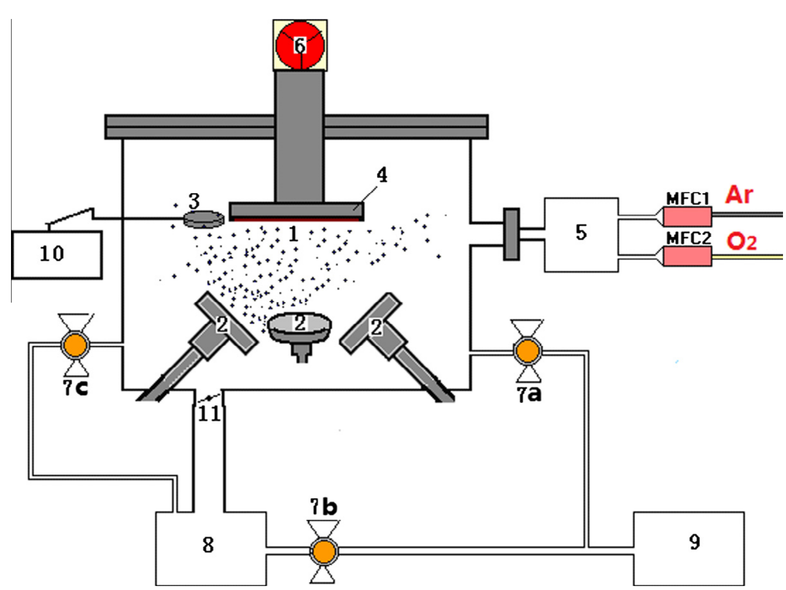

Fig. 1. Schematic diagram of the magnetron sputtering system (substrate-1, magnetron sources-2, quartz microbalance-3, resistive heater-4, gas supply-5, turning network-6, small angle valves-7a, 7b and 7c, molecular pump-8, mechanical pump-9, frequency meter-10, parallel slide valve-11).